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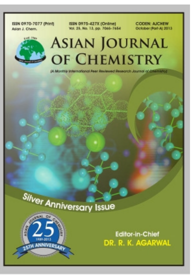

Synthesis and Characterization of Diaryl Pyrazole-4-carbaldehyde Semicarbazones Metal Complexes

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Four heterocyclic ligands [1,3-diarylpyrazole-4-carbaldehyde semicarbazones] and their metal complexes with *d*-block transition elements (Cu^{2+}, Ni^{2+}, Co^{2+}, Pb^{2+}, Zn^{2+} and Fe^{2+}) have been synthesized and characterized through elemental analysis and spectroscopic techniques *viz.*, FTIR, ^1H NMR and mass spectra.

Key Words: Semicarbazones, Vilsmeier-Haack reaction, *d*-Block metal complexes, Pyrazoles and NMR spectra.

INTRODUCTION

Semicarbazones are commonly used as ligands in coordination chemistry and are biologically active compounds. Their complexation with different metals enhances the bioactivity of these molecules. These metal based complexes have attracted considerable interest in chemical and biological studies due to their potentially beneficial biological activities which may be attributed to formation of their chelates with metal ions[1-8]. In continuation of our previous studies of the metal complexes of diphenylpyrazole compounds[9-12], we would now like to report the synthesis of some novel metal complexes of diverse 1,3-diarylpyrazole-4-carbaldehydes semicarbazones.

EXPERIMENTAL

AR grade chemicals purchased from Merck and Aldrich were used in this study. The ^1H NMR spectra were recorded on Varian MR Instrument at 300 MHz in $CDCl_3$ using tetramethylsilane (TMS) as internal standard. Electron spray ionization mass spectra (ESI MS) were recorded on VG AutoSpec M series (EBE) MS spectrometer. FTIR spectra were recorded on Bruker Tensor-27. Elemental analyses were performed using Carlo Erba 1106 automatic analyser. Melting points were taken on a GallenKemp melting point apparatus and are uncorrected.

1,3-Diarylpyrazole-4-carbaldehydes (1 and 2): Synthesis of ligands **1** and **2** has already been reported in a previous publication[12].

1,3-Diarylpyrazole-4-carbaldehyde semicarbazones (3 and 4): General method: A mixture of 1,3-diarylpyrazole-4-carbaldehyde (5 mmol), semicarbazide hydrochloride (5 mmol) and 3-4 drops of phosphoric acid in ethanol (35 mL), was refluxed for 45 min. After cooling, the mixture was poured into distilled water (200 mL), off white precipitates were filtered off and recrystallized from ethanol.

The following semicarbazones were prepared in this manner.

1,3-Diphenylpyrazole-4-carbaldehyde semicarbazone (**3**) Off white crystals, m.p. 202 ºC, yield; 1.4 g; 77%.

3-(4′-Chlorophenyl)-1-phenylpyrazole-4-carbaldehyde semicarbazone (**4**) Off-white crystals, m.p. 208 ºC, yield; 1.7 g; 85 %.

Synthesis of metal complexes (5-16): General method: Metal(II) chlorides (1 mmol) were dissolved in 10 mL ethanol and the solution was mixed with a warm ethanolic solution (25 mL) containing equimolar quantity (1 mmol) of ligands (**3** or **4**). The mixture was refluxed for 4 h, cooled to room temperature and poured into distilled water (200 mL) to give crystalline precipitates. These were washed successively with water and ethanol, dried by vacuum suction and stored in a desiccator containing anhydrous calcium chloride. The physical and spectral data of complexes is tabulated in Tables 1 and 2.

RESULTS AND DISCUSSION

Scheme-I gives the general method for the synthesis of the semicarbazones ligands **3** and **4**. These were obtained in good yields (70-75 %) by the condensation of warm ethanolic solutions of corresponding aldehydes and semicarbazide. Elemental analysis, mass spectra, FTIR and ^{1}H NMR were used to confirm the formation of respective complexes. Physical and Spectral data are tabulated in Tables 1 and 2.

Various metal complexes (**5-16**) were prepared and characterized through their elemental analysis and spectroscopic data. Atomic absorption spectroscopy was used to determine the metal contents of these complexes and metal to ligand ratio was found to be 1:2. This ratio was also confirmed from mass spectral data and elemental analysis (CHN).

FTIR analysis: The mode of bond formation in complexation between ligand and metal ions can be effectively determined by the FTIR spectra (Table-2). The enolic forms of the ligands (semicarbazones) seem to be more dominant than the ketonic tautomeric forms. This is substantiated by the presence of a broad OH absorption band for the ligands (**3** and **4**) in the region of 3500-3000 cm^{-1} which is absent in all the complexes (**5-16**) pointing to an enolic O-bonding to the metal while there is a discreet shift in the carbonyl frequencies of the semicarbazone ligands (**3** and **4**) as compared with their corresponding metal complexes. The characteristics peaks for NH_2 are observed[13] at 3500-3000 cm^{-1}. The absorption bands around 1660-1590 cm^{-1} are designated to the azomethine

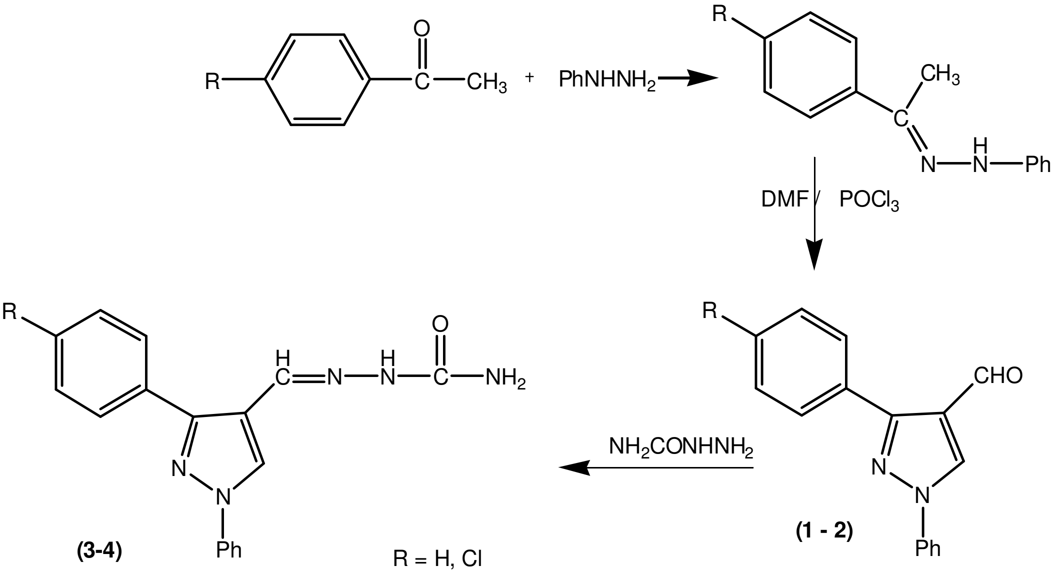
TABLE-1
PHYSICAL DATA FOR THE LIGANDS AND THE METAL COMPLEXES

Compd.	Yield (%)	m.p. (ºC)	MS†	m.f.	Elemental analysis (%) Calcd. (Found)			
					M	C	H	N
3	88	194	305**	$C_{17}H_{15}N_5O$	–	66.87 (66.82)	4.95 (4.92)	22.94 (22.91)
5	78	266 *	673	$C_{34}H_{30}N_{10}O_2Cu$	9.43 (9.28)	60.57 (60.53)	4.48 (4.52)	20.77 (20.71)
6	76	241*	668	$C_{34}H_{30}N_{10}O_2Ni$	8.77 (8.62)	61.01 (61.03)	4.52 (4.57)	20.93 (20.89)
7	76	257*	669	$C_{34}H_{30}N_{10}O_2Co$	8.80 (8.65)	66.99 (66.92)	4.52 (4.49)	20.92 (20.89)
8	82	234*	818	$C_{34}H_{30}N_{10}O_2Pb$	25.33 (25.20)	49.93 (49.95)	3.70 (3.73)	17.13 (17.15)
9	74	243*	674	$C_{34}H_{30}N_{10}O_2Zn$	9.67 (9.55)	60.40 (60.43)	4.47 (4.49)	20.72 (20.75)
10	74	251*	666	$C_{34}H_{30}N_{10}O_2Fe$	8.38 (8.24)	61.27 (61.31)	4.54 (4.51)	21.01 (21.05)
4	85	199	339**, 341	$C_{17}H_{14}N_5OCl$	–	60.09 (60.02)	4.15 (4.08)	20.61 (20.63)
11	73	249*	741, 743	$C_{34}H_{28}N_{10}O_2CuCl_2$	8.55 (8.41)	54.95 (54.87)	3.80 (3.74)	18.85 (18.84)
12	74	251*	736, 738	$C_{34}H_{28}N_{10}O_2NiCl_2$	7.95 (7.78)	55.32 (55.25)	3.82 (3.71)	18.97 (18.93)
13	72	247*	737, 739	$C_{34}H_{28}N_{10}O_2CoCl_2$	7.98 (7.81)	55.30 (55.37)	3.82 (3.85)	18.97 (18.83)
14	72	262*	886, 888	$C_{34}H_{28}N_{10}O_2PbCl_2$	33.37 (33.24)	46.05 (46.11)	3.18 (3.14)	15.80 (15.87)
15	68	246*	742, 744	$C_{34}H_{28}N_{10}O_2ZnCl_2$	8.78 (8.59)	54.82 (54.87)	3.79 (3.81)	18.80 (18.77)
16	64	258*	734, 736	$C_{34}H_{28}N_{10}O_2FeCl_2$	7.59 (7.41)	55.53 (55.46)	3.84 (3.82)	19.05 (19.01)

*Decomposed; **Corresponding to [L$^+$].

TABLE-2
FTIR AND ^{1}H NMR DATA

Compd.	IR (cm^{-1})	^{1}H NMR data δ (ppm)
3	3340.8 (NH2), 3176.4 (OH), 1664.8 (C=O), 1587.7 (C=N-N=C)	^{1}H: 10.05 (s, 1H, NHCO), 9.24(s, 1H, CH=N), 8.28 (s, 1H, Pz), 7.26-7.83 (m, 10H, Ar), 5.51 (s, br, 2H, NH_2)
5	3353.7 (NH_2), 1663.5 (C=O), 1591.1 (C=N-N=C)	–
6	3351.8(NH_2), 1666.6 (C=O), 1585.8 (C=N-N=C)	^{1}H : 9.23 (s, 1H, CH=N), 8.26 (s, 1H, Pz), 7.26-7.80 (m, 10H, Ar), 5.50 (s, br, 2H, NH_2)
7	3357.7(NH_2), 1683.7 (C=O), 1592.1 (C=N-N=C)	^{1}H : 9.57(s, 1H, CH=N), 8.35 (s, 1H, Pz), 7.26-7.98 (m, 10H, Ar), 5.90 (s, br, 2H, NH_2)
8	3309.7 (NH_2), 1667.9 (C=O), 1594.8 (C=N-N=C)	^{1}H : 8.89 (s, 1H, CH=N), 8.28 (s, 1H, Pz), 7.26-7.79 (m, 10H, Ar), 5.10 (s, br, 2H, NH_2)
9	3315.7(NH_2), 1668.7 (C=O), 1591.8 (C=N-N=C)	^{1}H : 9.04 (s, 1H, CH=N), 8.28 (s, 1H, Pz), 7.26-7.80 (m, 10H, Ar), 5.75 (s, br, 2H, NH_2)
10	3361.6 (NH_2), 1670.8 (C=O), 1589.7 (C=N-N=C)	–
4	3463.8 (NH_2), 3287.2 (OH), 1682.8 (C=O), 1594.8 (C=N-N=C)	^{1}H: 8.42 (s, 1H, NHCO), 8.29(s, 1H, CH=N), 8.14 (s, 1H, Pz), 7.26-7.78 (m, 9H, Ar), 4.95 (s, br, 2H, NH_2)
11	3470.8 (NH_2), 1697.0 (C=O), 1596.1 (C=N-N=C)	–
12	3491.3 (NH_2), 1687.6 (C=O), 1589.1 (C=N-N=C)	^{1}H : 8.27(s, 1H, CH=N), 8.16 (s, 1H, Pz), 7.27-7.79 (m, 9H, Ar), 4.50 (s, br, 2H, NH_2)
13	3472.9 (NH_2), 1695.8 (C=O), 1590.9 (C=N-N=C)	^{1}H : 8.26(s, 1H, CH=N), 8.13 (s, 1H, Pz), 7.27-7.79 (m, 9H, Ar), 4.71 (s, br, 2H, NH_2)
14	3470.4 (NH_2), 1698.8 (C=O), 1596.7 (C=N-N=C)	^{1}H : 8.28(s, 1H, CH=N), 8.11 (s, 1H, Pz), 7.25-7.74 (m, 9H, Ar), 4.55 (s, br, 2H, NH_2)
15	3472.3 (NH_2), 1699.2 (C=O), 1598.2 (C=N-N=C)	^{1}H : 8.20(s, 1H, CH=N), 8.11 (s, 1H, Pz), 7.28-7.76 (m, 9H, Ar), 4.45 (s, br, 2H, NH_2)
16	3479.6 (NH_2), 1700.3 (C=O), 1597.3 (C=N-N=C)	–



Scheme-I

(C=N-N=C) group[14]. In the complexes, the frequencies of azomethine groups appear mostly towards the lower region which strongly indicates that the ligands coordinate to the metal through the carbonyl oxygen and the azomethine nitrogen of the enolic form of the ligand (Fig. 1). This is further confirmed on the basis of ^{1}H NMR studies. Hence, the ligands act as monobasic bidentate ligands in all the complexes.

^{1}H NMR spectra: The chemical shift values for the ligands (**3** and **4**) and the metal complexes are recorded in Table-2. The two ligands differ only in substitution at 4′-position on the 3-aryl substituent in the pyrazole (Pz) ring. The 3-aryl ring protons show multiplets in the 7.20-7.98 ppm region. The characteristic NHCO signal, observed at 10.06 ppm (**3** and **4**), is conspicuously absent in all the metal complexes (**5-16**). A broad signal corresponding to -NH_2 group in ligands and complexes was also observed between 4.5-6.4 ppm[13] and a shift is observed in formation of these complexes. It was further observed that the signals of the protons at NHCO, H-5 proton of pyrazole (Pz) and 4′-substituted phenyl ring were shifted from their original δ values from the respective ligands (Table-2). Thus in the formation of complexes of these bivalent metal ions, the NHCO signals disappeared due to enolization of the ligands during complex formation with the help of the carbonyl carbon and azomethine nitrogen of the enolic tautomer **I** (Fig. 1).

Electron spray ionization mass spectra: The positive ion ESI MS of the ligands (**3** and **4**) and their metal complexes (**5-16**) in MeOH are dominated by the parent molecular ion peaks. The m/z values shown in Table-1 are L^+ molecular ion peak for ligands (L for ligands) and monopositive complex ion $[ML_2 + 2H]^+$ molecular ion peaks. The data support the assumption that metal to ligand ratio is 1:2 in all the complexes.

Conclusion

The present study revealed that the complexes formed from ligands (**3-4**) have stoichiometry of 2:1 (ligand:metal) with a possible structure showing chelation through carbonyl oxygen and azomethyne nitrogen structure **I** rather than structure **II** (Fig. 1). These are evidenced by their IR, ^{1}H NMR and elemental analytical data.

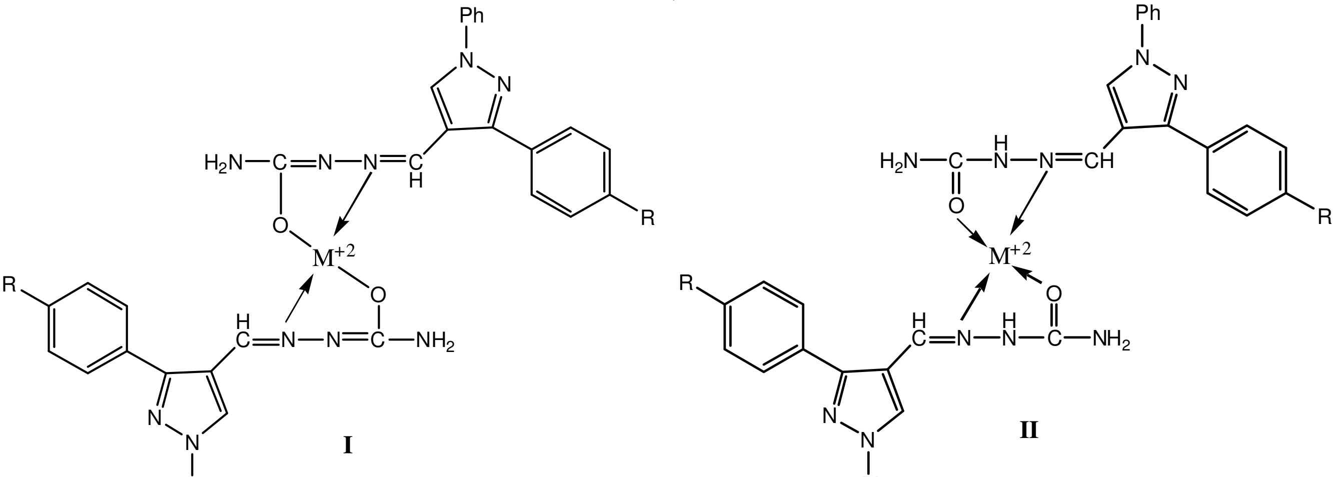


Fig. 1. Structure of metal complexes (**5-16**), R = H, Cl

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